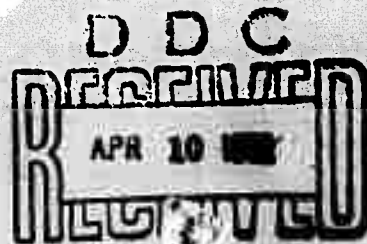FINAL TECHNICAL REPORT
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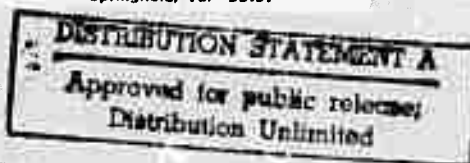
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13. ABSTRACT

The preparation of anomalous materials by condensation in five capillaries was investigated under varied conditions of temperature, pressure and atmospheric composition. These experiments indicated that a saturated atmosphere of water vapor and a relatively high area of glass surface are primary requisites. Attempts were made to form anomalous materials by condensation on glass wool. During a methanol experiment of this type, sodium methylcarbonate was isolated. It was concluded that the interaction of the room air (particularly the carbon dioxide) with the liquid and glass is important in the formation of anomalous substances. Attempts to condense anomalous materials directly from the air onto cold surfaces were somewhat successful with glass surfaces but not with plastic surfaces. This emphasized the role of glass. Further experiments with glass wools showed that anomalous materials may be prepared by the interaction of liquids with glass.

A possible explanation for the formation of anomalous materials on glass surfaces is that the first drops of liquid on the surface form basic sites which then condenses acidic substances from the air (primarily CO_2) to form salts. Small amounts of silicon compounds may be involved to help produce the anomalous properties.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Infrared spectrum, anomalous materials, anomalous water, glass, quartz, Pyrex, condensation, capillary, methanol, glass wool, carbonates, silicate.						

DD FORM 1473 (BACK)
(PAGE 2)

CORRECTION SHEET

Page iii, Line 4--- five to fine.

Page 4, Line 20--- pipe to pipet.

Page 40, Line 11--- unreasonable to reasonable.

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The purpose of this research was to explore the mechanism for the production of anomalous materials.

The preparation of anomalous materials by condensation in fine capillaries was investigated under varied conditions of temperature, pressure and atmospheric composition. These experiments indicated that a saturated atmosphere of water vapor and a relatively high area of glass surface are primary requisites. Attempts were made to form anomalous materials by condensation on glass wool. During a methanol experiment of this type, sodium methylcarbonate was isolated. It was concluded that the interaction of the room air (particularly the carbon dioxide) with the liquid and glass is important in the formation of anomalous substances. Attempts to condense anomalous materials directly from the air onto cold surfaces were somewhat successful with glass surfaces but not with plastic surfaces. This emphasized the role of glass. Further experiments with glass wools showed that anomalous materials may be prepared by the interaction of liquids with glass.

A possible explanation for the formation of anomalous materials on glass surfaces is that the first drops of liquid on the surface form basic sites which then condenses acidic substances from the air (primarily CO_2) to form salts. Small amounts of silicon compounds may be involved to help produce the anomalous properties.

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ABSTRACT

The nature of the formation of anomalous substances from the condensation of water (and other hydrogen bonding liquids) on glass was investigated. Several conditions for the formation are presented. A theory is proposed and discussed in relation to evidence from this investigation and the reported findings of other workers.

INTRODUCTION AND BACKGROUND

Ten years ago Fedyakin described a fluid which condenses from water vapor inside fine glass capillaries and possesses properties different from pure water. Since that time, the preparation,[2,3,4] physical properties,[1,4,5,6,8] chemical properties[7,8] and possible molecular structure[8,9,10,11] of this anomalous material have been investigated. The names water II, "polywater," and anomalous water have been used to suggest that this material is a hitherto unknown molecular form of water.

The physical measurements, including vapor pressure, density, refractive index, conductance, viscosity, molecular weight, thermal expansion upon freezing and stability at high temperature, have been made on minute amounts of material (estimated 10^{-6} to 10^{-8} g). In most cases, the material was still inside the tiny capillaries in which it formed. Mass spectrometric analyses were made on samples distilled from the tubes. Deryagin[5a] and Willis[6] reported masses corresponding to normal water and none indicating polymers of H_2O. The Russian work reported the presence of some organic impurities in the mass spectrum but they have not published a complete chemical analysis.

In much of the work on anomalous water, including that in this laboratory, the main criteria for selecting material for study have been the method of formation and the spectroscopic properties. The preparations usually employ glass or quartz surfaces exposed to vapors of water of other liquids under investigation. The infrared analysis gives a spectrum

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strong band near 1595cm^{-1} and a doublet near 1400cm^{-1}. The intensity of these bands has varied with samples from different sources but their presence has remained the chief indicator of whether the material was akin to that described by Deryagin et al.

Preparations in small capillaries have never yielded enough material so that several independent studies could be made on the same sample. Many workers have reported obtaining viscous liquids giving infrared absorption similar to that published by Lippincott, et al.[12] but containing significant amounts of organic and/or inorganic impurities. Yet efforts to synthesize a material possessing all the properties of anomalous water from known chemicals have not succeeded. It is clear that many samples of anomalous water contained significant amounts of identifiable "contaminants," but questions remain unanswered. Are these "contaminants" and the anomalous material the same thing? Is there a mechanism common to all the experiments producing anomalous material which accounts for the major portion of the product?

The purpose of this research is to explore the mechanism for the production of anomalous materials and to prepare sufficient quantities of the materials to characterize them chemically and to assess their technological utility.

Capillary Tubes

Atmosphere Variation

The most commonly reported method of preparing anomalous water has been to allow water vapor to condense slowly in Pyrex or quartz capillary tubes contained in a closed system. We decided to attempt to determine the effect of the composition and pressure of the gas in the closed system upon the amount of anomalous material formed.

The thin Pyrex tubes used for these experiments had an outer diameter between 75 and 150μ and a bore between 1 and 30μ. They had been pulled in a specially constructed machine, then baked in a stream of oxygen before exposure to a saturated water vapor atmosphere. This treatment was handled in such a manner that these tubes were not exposed to human handling. In earlier experiments with some of these tubes, it was observed that when placed in an atmosphere of saturated water vapor, close to 100% of the tubes tested positive. A tube was considered positive if when removed from the atmosphere of water vapor and viewed at X70 magnification, a visible column of material was observed.

The desiccators used in these experiments were equipped with O-rings and Teflon stopcocks. Each was washed in hot soapy water, carefully rinsed in hot water and distilled water and dried in an oven at 70°C. Pyrex dishes, used to hold the capillaries, were similarily washed with the addition of a final rinse in 30% hydrogen peroxide. Plastic gloves or tongs were used for all handling.

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were used. About 200ml of distilled water was poured in the bottom of each desiccator and a covered pyrex dish containing several hundred of the capillaries was placed on the shelf above the water. All three desiccators were pumped down with a water aspirator to about 40mm of Hg. No additional gases were added to the first desiccator. Pure dry CO_2 was added to the second until there was a positive pressure inside the desiccator. The third desiccator was filled with 0.5% carbon monoxide in helium. Each day, for five days, ten or more capillaries were removed from each desiccator and examined under a microscope. After each sampling the desiccators were pumped down and gases added as before. The results are given in Table 1.

Since the results showed no tubes were filled at atmospheric pressure, a second experiment was devised to test the affect of varying the pressure. The three desiccators used earlier were rewashed and filled with fresh capillaries and water as before. In this experiment, after the desiccators were pumped down, they were filled with gases from a gas pipe and the pressure was measured with a manometer. Desiccators 1 and 2 had water vapor and carbon dioxide, respectively, added as before. Pure carbon monoxide was used in desiccator 3 instead of the mixture with helium. A fourth desiccator (glass equipped with an O-ring and teflon stopcock) was added for this experiment. An erlenmeyer flask with concentrated nitric acid was placed beside the capillaries and the pressure was varied by controlling the pump down. The test for positive

TABLE 1. Effect of Atmosphere on the Formation of Material in Capillary Tubes. Experiment 1.

Day	Desiccator 1. Water vapor evacuated to 40 mm. % positive tubes	Desiccator 2. Water vapor evacuated to 40 mm. Pure dry CO_2 added to atmospheric pressure. % positive tubes	Desiccator 3. Water vapor evacuated to 40 mm. 0.5% CO in He added to atmospheric pressure. % positive tubes
1	100	0	0
2	50	0	0
3	60	0	0
4	66	0	0
5	100	0	0

The results of the experiments seem to indicate that there is no relationship between the number of filled tubes and the composition of the atmosphere. There does not seem to be any clear connection between the pressure of the atmospheres and the number of filled tubes. While some difficulty was experienced in obtaining material with atmospheric pressure, this is thought to be due to a poor seal on the desiccator resulting in a less than saturated water vapor content. The desiccator covers do not provide seal unless there is some reduction of pressure on the inside.

A few experiments were carried out to see whether there was any difference in the material formed in the tubes kept under different gases. Neither prolonged pumping nor heating revealed any difference in the time required to remove the liquid columns from the capillaries of the four desiccators.

Large Preparation

Since it has been reported[5] that anomalous water can be distilled, we decided to attempt to prepare a significant amount of the material by distilling the contents of a large number of capillaries into one vessel. Several thousand (estimated about 10,000) of the tubes described in the previous section were placed in a tube equipped with vacuum O-ring seal. The tube full of capillaries was suspended over water in a desiccator for about one week. It was then removed and attached to a vacuum line. The tubes were gently heated and the chamber was continuously pumped through a cold trap. Several

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TABLE II. Effect of Atmosphere on the Formation of Material in Capillary Tubes. Experiment 2.

Day	Desiccator 1. Water Vapor Pressure mm Hg	% positive	Desiccator 2. CO_2 Pressure mm Hg	% positive	Desiccator 3. CO Pressure mm Hg	% positive	Desiccator 4. Pressure mm Hg
1	37	100	137	75	144	100	420
2	50	87	122	86	140	100	218
3					156	57	85
4	100	100			750	0	
9	750	50	146	88	140	22	360
11			111	92	145	62	167
16	434	33	522	33	85	72	108
17	56	85	84	62	103	53	60
18	750	28	101	57	110	77	760
19	39	83	39	100	55	92	48
22	35	71	760	88	725	89	760
23	760	0	760	67	500	75	500
24	760	0	760	12			760

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hours, however, all of the liquid evaporated.

We concluded that either no anomalous material was formed or it could not be distilled in this manner. No further experiments of this type were performed.

Temperature Elevation

A process in which acid-treated Pyrex or quartz capillary tubes are kept at slightly higher than normal temperature in an evacuated container, in the presence of water and water vapor, was privately reported to us to repeatedly yield material in fair amounts. This material reportedly consistently gave the infrared spectrum of anomalous water.

In this experiment, glass tubing was soaked in concentrated nitric acid, allowed to drain for two days, and baked in an oven at 110°C for a day. The tubing was then drawn into capillaries with a bore less than 150μ. The capillaries were placed in a petri dish covered with a watch glass. The dish was suspended over water in an evacuated aluminum desiccator that was heated to 30°C. After several days, the desiccator was opened and the tubes examined. Droplets had condensed on the watch glass and on the petri dish but little or no material was observed in the capillaries.

In order to facilitate the contact of the water vapor with the capillaries, the experiment was repeated with the watch glass suspended above the petri dish upon a small glass triangle. When the desiccator was opened this time, several droplets of water had collected in the petri dish and a number of the capillaries contained material. However, when the

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spectrum, a large amount of it evaporated. Out of twelve
experiments, only three gave yields of anomalous-like materials
and in these instances, the yields were very low.

Pyrex Wool

Since most all of the reported methods for the formation
of anomalous water used quartz or Pyrex surfaces, it is reason-
able to suspect that silicon may be important in its formation.
If silica is involved, it can be expected that suitable treat-
ment of high surface area forms of silica might lead to sub-
stantial amounts of anomalous product. Therefore, attempts
were made to produce anomalous water with the use of glass wool.

A batch of Corning Pyrex wool, free of coating, was
treated in a five step process:

1. Heated on a steam bath for two hours in concentrated
nitric acid

2. Washed with deionized water until neutral and then
rinsed six more times.

3. Boiled in deionized water for ten minutes

4. Dried in air for twelve hours at $110°C$

5. Suspended over deionized water in a grease-free vacuum
desiccator for two days.

A portion of the glass wool (5g dry weight), treated as
above, was placed in a Buchner funnel and extracted by suction
with a water aspirator. Since only a few drops of liquid were
obtained, the wool was rinsed with 10ml of deionized water and
this was mixed with the material originally collected. The

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left a clear glassy residue. The infrared spectrum of this residue, Figure 1, shows main absorption bands at 1685, 1575, 1420 and $1100cm^{-1}$.

The following qualitative tests were carried on the filtrate:

Chloride test with $AgNO_3$ ---------------------- Negative
Sulfuric acid test for charrable material------Negative
Acidified $BaCl_2$ test for sulfate ion ----------Positive
HCl test for carbonate or bicarbonate ---------Positive

After treatment of the glassy film on the plate with hydrochloric acid, all of the infrared absorption bands, except the $1100cm^{-1}$ band, disappeared. On long standing or upon heating, the clear glassy residue changed to small white crystals.

Quartz Wool

A batch of quartz wool was treated similarly to the Pyrex wool in the previous section. The amount of anomalous material remaining after the rinse water was concentrated was much less than with Pyrex wool. The infrared spectrum indicated that the material formed from quartz wool was similar to that formed from Pyrex with the addition of a broad band centered around $1050cm^{-1}$. This band was thought to be due to a small amount of silicate impurity in the quartz prepared sample.

Methanol

Pyrex Wool

Since washing of treated wool with water leads to the possibility of forming anomalous water in the process, it was
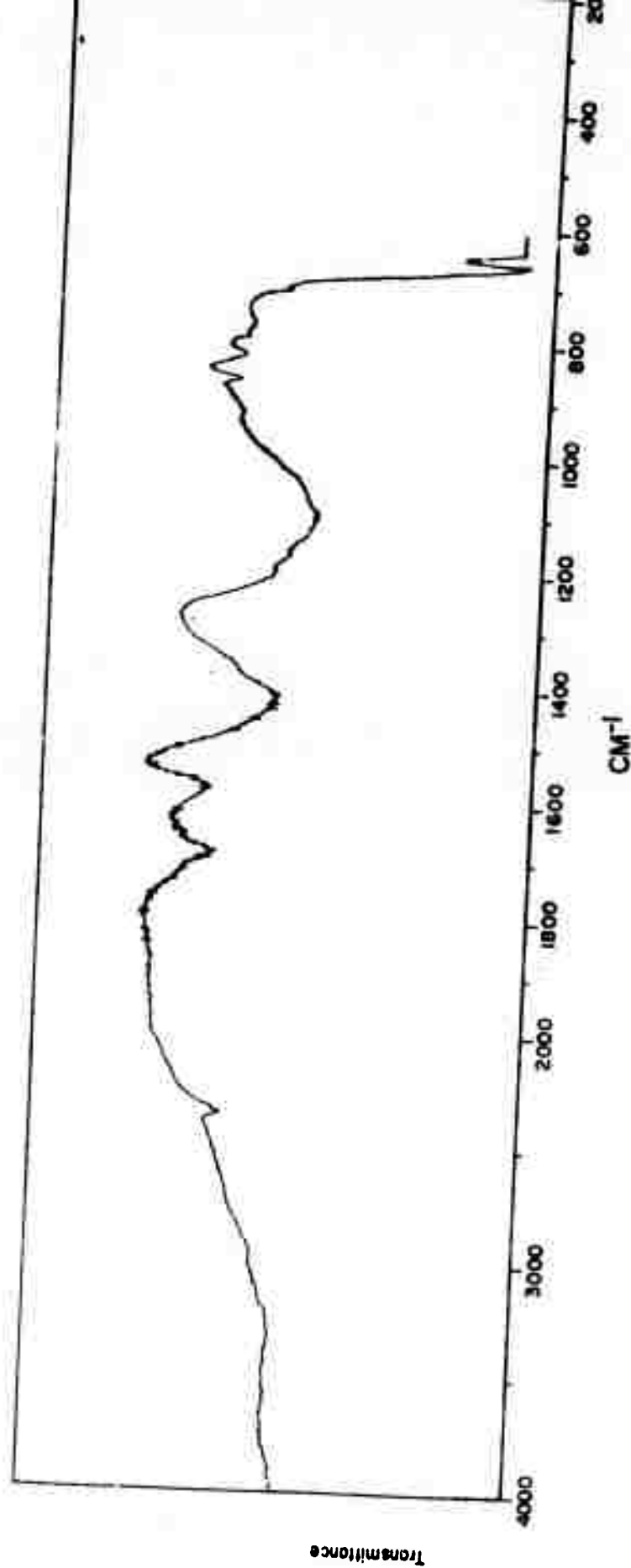
Figure 1. Infrared spectrum of a water extract of Pyrex wool.

Transmittance

CM⁻¹

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at which step the anomalous material was formed, inorganic impurities on the glass surface should be less soluble in methanol.

A portion of the Pyrex wool, treated as described earlier, was stuffed into a glass column 60 cm long by 2 cm inside diameter. A space approximately 20cm long was left above the wool. The bottom of the column was equipped with a sintered glass plate and a Teflon stopcock. Care was taken to handle the wool only with plastic gloves or a glass stirring rod.

The wool was rinsed with about 20ml of spectral-grade absolute methanol. The rinsings were collected and poured through the glass wool about ten times. In most cases, the filtrate was quite clear and no further filtration was needed. The filtrate was concentrated in an evacuated desiccator with drierite and calcium chloride. When the liquid was evaporated to dryness, a white solid remained. It was observed that not all of the solid would redisolve in the original volume of alcohol.

The infrared spectrum of the solid residue, taken on an Irtran plate, is shown in Figure 2. It bears some resemblance to the published spectra for anomalous water and those of bicarbonate and carbonate ions. The bands around $2900 cm^{-1}$, commonly associated with C-H stretching, are at different frequencies from those in methanol and the O-H stretching mode observed in methanol at $3400 cm^{-1}$ is absent in Figure 2. Also the O-H stretching absorption of bicarbonate ion is not observed. The spectrum of the residue is compared to that of sodium bicarbonate,
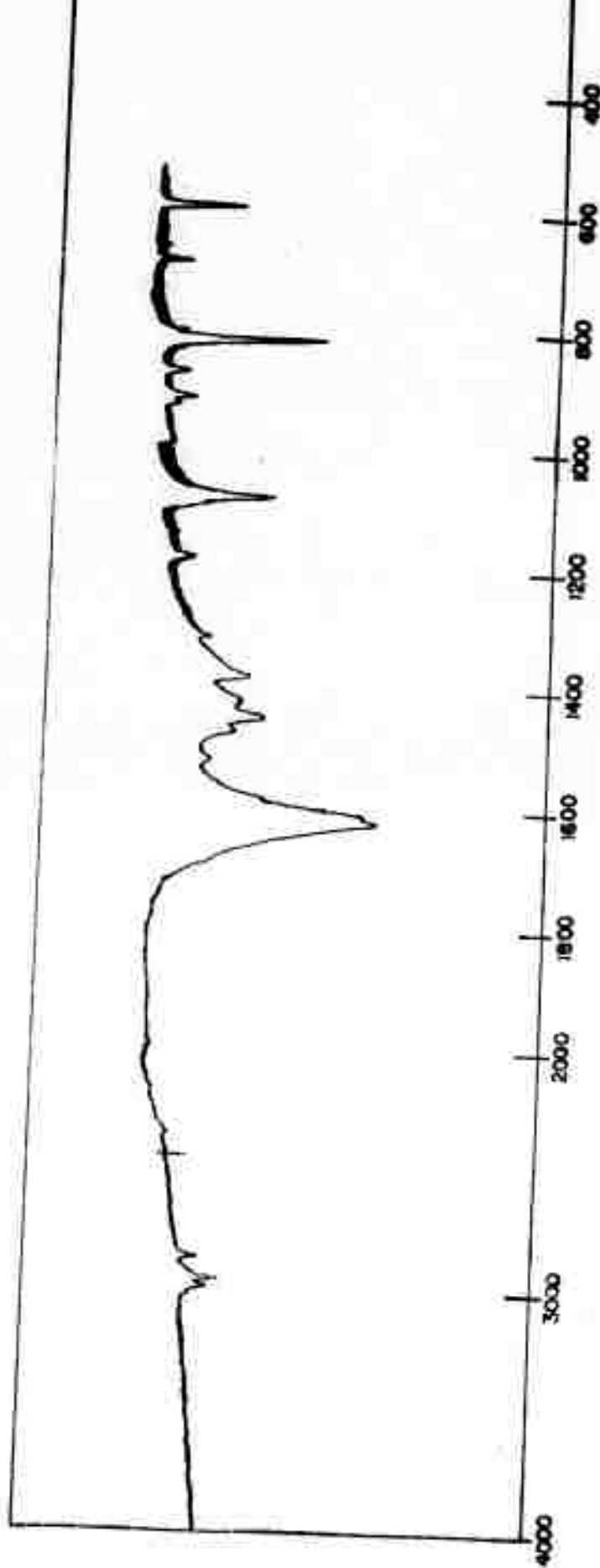
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Figure 2. Infrared spectrum of a methanol extract of Pyrex wool.

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sodium carbonate and methanol in Table III.

When the residue was placed in a warm dry atmosphere, in the purged sample compartment of a Perkin-Elmer 225 infrared spectrometer under a continuous stream of dry air, the bands at 1425 and $875 cm^{-1}$ increased in intensity, while the other major bands decreased correspondingly. In a similar way, when 5% sodium hydroxide solution is added to the residue, the 1425 and $875 cm^{-1}$ bands become stronger. These changes indicate a reaction to form sodium carbonate.

Sodium Bicarbonate-Methanol

In order to ascertain whether a substance like the residue from methanol washings of treated glass wool could be prepared without the presence of glass wool, methanol solutions of bicarbonates were studied. This was suggested by the presence of bicarbonate in the residue. It was found that if a saturated solution of sodium bicarbonate in methanol is allowed to evaporate to dryness, a white residue remains. The infrared spectrum of this residue is identical to that of the residue formed from the methanol washings of treated wool (Figure 2).

Characterization

Since a computer search of Sadtler's files of infrared spectra did not turn up a match for the spectrum of the methanol-bicarbonate product, several experiments to characterize some of its properties were run.

When samples of the residue were dried in a desiccator to a constant weight, and then heated in an oven at 110°C for several hours, an average weight loss of 45% was observed.

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TABLE III. Comparison of the Infrared Frequencies of NaCH₃CO₃, MeOH, NaHCO₃, Na₂CO₃

NaHCO₃ – MeOH residue (NaCH₃CO₃) Infrared cm⁻¹	rel. int.	Raman cm⁻¹	rel. int.	MeOH (liquid) Infrared cm⁻¹	rel. int.	NaHCO₃ [2] (solid) Infrared cm⁻¹	rel. int.	Na₂CO₃ (solid) Infrared cm⁻¹	rel. int.
				3337	vs	3050	m		
3010	vw	3020	w						
2982	w	2990	w						
2950	w	2951	s	2934	vs	2910	m	2930	vw
2860	w	2863	m	2822	s				
				2571	w	2620	s		
				2502	w	2540	s	2560	vw
				2340	vw	2460	s	2495	w
				2232	vw				
				2053	w	1920	w		
						1830	w		
1690	vw					1693	m		
1625	s	1630	vw			1659	vs		
1612	s					1616	vs		
1585	m								
1473	w	1465	w	1480	sh				
1452	m	1450	s	1455	m	1448	s	1451	vs
		1435	s						
1382	m	1360	m	1420	m	1395	vs		
						1300	vs		
1185	w	1172	m	1114	w				

TABLE III. Comparison of the Infrared Frequencies of NaCH$_3$CO$_3$, MeOH, NaHCO$_3$, Na$_2$CO$_3$ (continued)

NaHCO$_3$ - MeOH residue (NaCH$_3$CO$_3$)				MeOH[1] (liquid)		NaHCO$_3$[2] (solid)		Na$_2$CO$_3$ (solid)	
Infrared cm^{-1}	rel. int.	Raman cm^{-1}	rel. int.	Infrared cm^{-1}	rel. int.	Infrared cm^{-1}	rel. int.	Infrared cm^{-1}	rel. int.
1100	vw	1140	w						
1082	m	1090	w						
		1070	w	1029	vs	1046	m	1079	vw
						1036	m		
						998	s		
918	w	920	vs						
820	s	816	w			837	s	881	s
805	w					795	vw	855	w
688	vw	685	m	655	s	700	vs	701	w
						690	vs	694	w
593	w	595	s			650	m		

The letters w, m, s, v and sh mean weak, medium, strong, very and shoulder, respectively.

[1] M. Falk and E. Whalley, J. Chem. Phys., 34 1554 (1961).

[2] A. Novak, P. Saumagne and L. D. C. Bok, J. Chim. Phys., 60 1385 (1963).

[3] K. Buijs and C. J. H. Schutte, Spectrochim. Acta, 17 927 (1961).

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It was found that the samples had generally reached a constant weight after an hour in the oven and little weight change was observed even with prolonged heating. A few samples were further heated to 300°C and no additional weight loss was observed.

Carbon and hydrogen analyses were obtained. The average values were 22.25% and 2.38% for carbon and hydrogen, respectively. However, if the residue is a type of bicarbonate, as the infrared spectral charges and the reaction to base indicate, these results should be considered low. Control samples of sodium bicarbonate were submitted along with the residue samples. The carbon and hydrogen percentages reported were 9.9% and 1.12 respectively (calculated: C - 14.28%, H - 1.19%).

A qualitative chromatographic analysis of some of the solid residue showed the presence of carbon dioxide, water, and methanol. When some of the solid was dissolved in ethanol and the solution analyzed, a peak was observed that corresponded to methanol.

Several samples of the residue from a saturated solution of sodium bicarbonate in methanol were titrated with 0.1N HCl. The average value of the titer was 0.0092g/ml. This compares with 0.0080g/ml for sodium bicarbonate and 0.0051g/ml for sodium carbonate.

A residue sample was prepared from a saturated solution of $NaDCO_3$ in CH_3OD. The infrared spectrum of this residue was identical to that of its non-deuterated analog.

The Raman spectrum of the solid residue from a saturated solution of sodium bicarbonate in methanol was recorded. The

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observed frequencies are listed in Table III. Comparison with the infrared frequencies shows the expected similarities. The presence of bands at the same frequency in the infrared and Raman spectra rules out a center of symmetry in the residue molecule.

The electron spectra of the residue was studied using a Varian IEE-15 Electron Spectrometer. The oxygen and sodium spectra showed electrons of only one energy while the carbon spectrum (Figure 3) showed electrons from carbons in at least two different environments. The lowest energy peak, 286.4eV, is the normal carbon impurity in the background and it is not certain whether it contains a contribution from the residue or not. The highest field peak is in the range generally associated with a carbonate type carbon while the middle energy is in the range of carbon bonded to an oxygen.

Other Alcohols

Saturated solutions of sodium bicarbonate in ethanol and in isopropanol were also prepared. The infrared spectra of the residues from these solvents were very similar to that of the residue from methanol. The main difference being in the region around $2900cm^{-1}$ generally associated with C-H stretching vibrations. The spectra of the three residues are compared in Figure 4.

Identity of Methanol-Bicarbonate Residue

The absence of band shifts in the infrared spectrum of the residue from the saturated solution of $NaDCO_3$ in CH_3OD shows that the deuterium atoms are eliminated in the reaction between
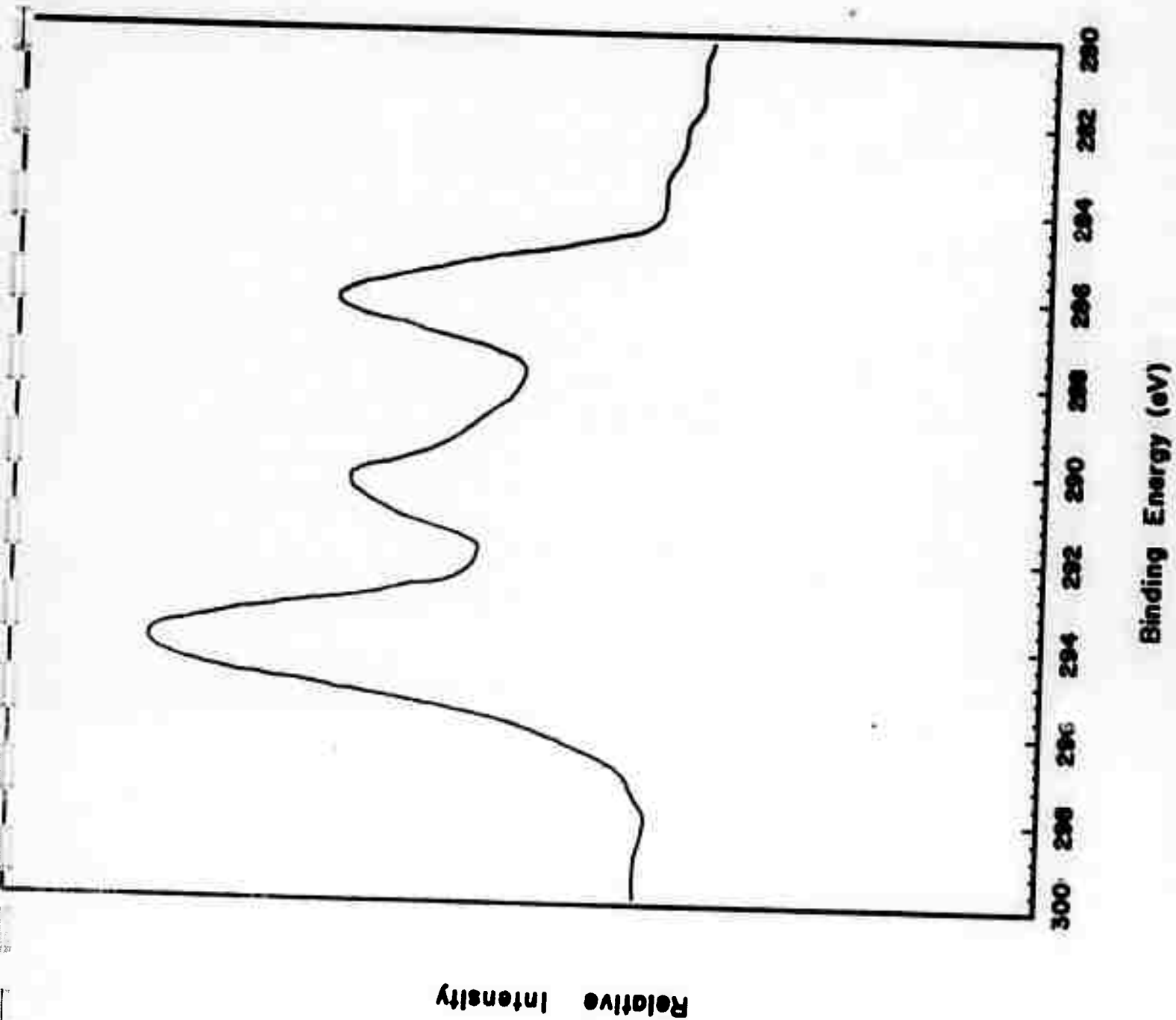
Figure 3. ESCA spectrum of the carbon region of a residue from a saturated solution of sodium bicarbonate in methanol.
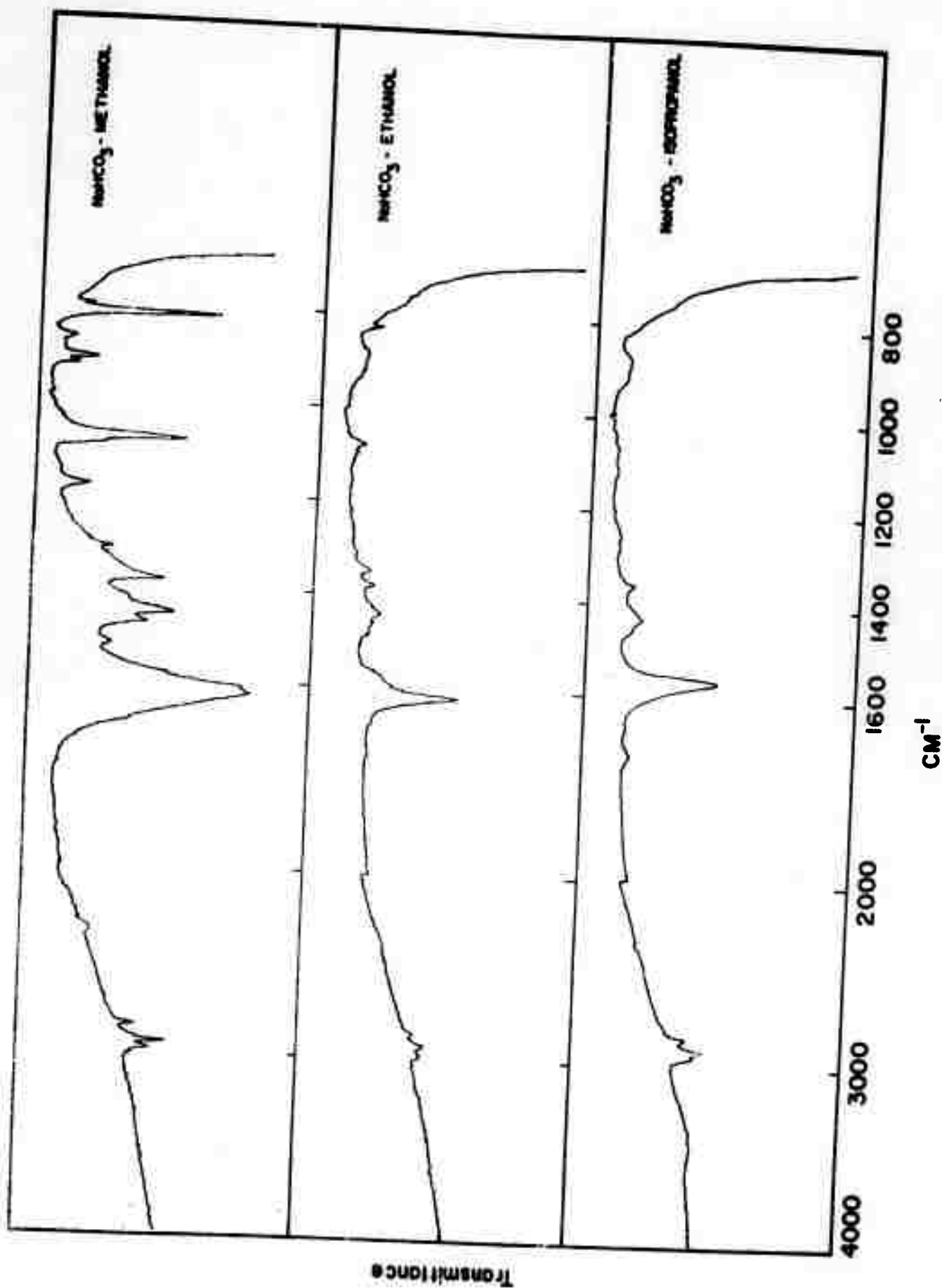
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Figure 4. Infrared spectra of residues from solutions of sodium bicarbonate in methanol, ethanol and isopropanol.

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the bicarbonate and the alcohol. The similarity of the spectrum of the residues from methanol, ethanol and isopropanol solutions of bicarbonate indicates a similar reaction of the three alcohols with the bicarbonate. The infrared spectra (bands in the 800, 1100, 1400, 1600 and $2900 cm^{-1}$ regions) indicate the residues are organic carbonate salts. A comparison of the spectrum of the residue from a solution of sodium bicarbonate in methanol with the Sadtler spectrum of sodium methylcarbonate shows a great deal of similarity. The match is almost perfect if contributions from methanol, water, sodium carbonate and sodium bicarbonate are subtracted from the Sadtler spectrum. The identification of the residue was confirmed by comparing its infrared spectrum and some of its properties to those of samples of sodium methylcarbonate prepared according to the procedure of J. J. Jones.[13] ($NaOCH_3 + CO_2 = NaCH_3CO_3$)

Decomposition of Sodium Methylcarbonate

During the course of experiments to identify sodium methylcarbonate it was observed that under certain conditions the compound decomposed. In some cases sodium methylcarbonate decomposed to form sodium carbonate and a compound characterized by bands at 2950(vvw), 2925(w), and 2850(w)cm^{-1}. In other instances the decomposition was more complex and the spectra somewhat resembled those attributed to anomalous water. Because of this similarity and the interesting appearance of the bands at 2950, 2925, and $2850 cm^{-1}$ (normally associated with the presence of CH_2 groups in the molecule) we conducted further studies on the decomposition of sodium methylcarbonate.

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Plates (some Irtran, some silver chloride) were prepared with a thin film of sodium methylcarbonate and the infrared spectra were recorded to check the purity. A plate was then placed in each of the following environments: exposed to room air in a covered petri dish; placed in a desiccator over drierite; placed in a desiccator over drierite and the desiccator evacuated; placed in a desiccator over drierite and the desiccator heated to 50°C; placed in a desiccator over water. The plates were removed and their infrared spectra were recorded periodically. The final spectra of these plates after four months of treatment are shown in Figure 5.

The plates in the dry desiccator (Figure 5b) and in the evacuated desiccator (Figure 5a) showed little decomposition. The weak bank at $880 cm^{-1}$ indicates the presence of a small amount of sodium carbonate. Also there are very weak shoulders at 2925 and $2850 cm^{-1}$. This appeared to be a direct transition since the bands of the final form increased in intensity over the period of observation as those of sodium methylcarbonate decreased. No bands of other compounds were observed. The spectrum of the sample stored in a moist atmosphere (Figure 5d) shows a complex mixture of carbonate type compounds. Sodium carbonate, sodium carbonate monohydrate, sodium bicarbonate and trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) can be identified. The bands observed at 2925 and $2850 cm^{-1}$ in the previous decompositions are only very weakly present in this sample. These bands were much more prominent in the earlier stages of the wet decomposition. Figure 5e is the spectrum of a sample of sodium methylcarbonate allowed to stand in air. The spectrum is somewhat similar to
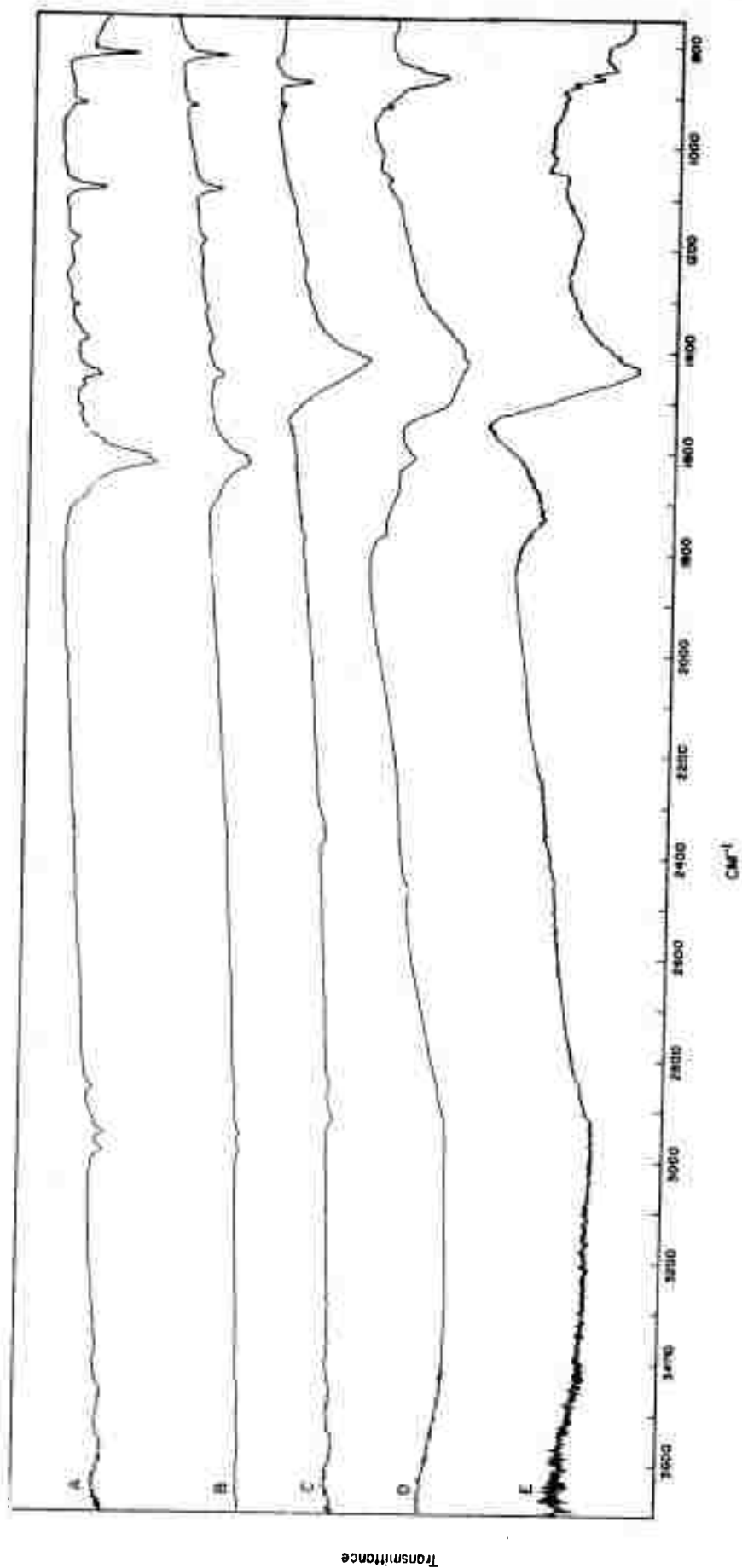
22

Figure 5. Infrared spectra of sodium methyl-carbonate after three months in: a) evacuated desiccator; b) desiccator over drierite; c) desiccator over drierite heated to 50°C; d) desiccator over water; e) covered petrie dish in room air.

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that of the wet decomposed sample (Figure 5d). The compounds present may tentatively be identified as sodium carbonate, sodium bicarbonate and sodium carbonate monohydrate. Again, in this sample the bands in the $2900cm^{-1}$ region are very weak.

While the previous explanation accounts for the majority of the spectral features there are still points that are not understood. Three of the spectra (Figure 5c, d, e) have an absorption in the 1700 to $1800cm^{-1}$ region. This is the region generally associated with the C=O stretch. The bands observed at 2925 and $2850cm^{-1}$ in the decomposed samples are also hard to explain. The explanation of chance organic impurities seems insufficient since the samples were treated in such different manners and the change in frequencies are the same in each case. All desiccators were greaseless and the only sample that was evacuated with a vacuum pump showed one of the least amounts of contamination. The chance of dust particles settling upon the samples seems remote since all samples were well-covered except during the time when the spectra were being recorded. Finally, the appearance of these bands corresponds somewhat with the disappearance of the methyl stretching bands of the sodium methylcarbonate.

Some further experiments on the decomposition were performed. A sample of sodium methylcarbonate was cast as a film onto a silver chloride plate. After the infrared spectrum was recorded, the plate was irradiated with 2537Å U.V. light for 24 hours. The infrared spectrum was recorded again and no appreciable sample decomposition was observed.

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A bulk sample of sodium methylcarbonate (as opposed to the thin films used earlier) was allowed to stand in air for 6 weeks. The infrared spectrum of the decomposed sample is shown in Figure 6. Except for the sodium carbonate bands, this spectrum is quite different from the earlier decompositions (Figure 5). The bands at 780, 1360, and $1600cm^{-1}$ may be due to an oxalate group however there are also bands at 1780, 2490, 2510, 2715, 2830 and $2950cm^{-1}$.

A water solution of sodium methylcarbonate was prepared and some was evaporated to dryness on a silver chloride plate. The infrared spectrum of the residue showed that the bulk of the sample remained unchanged while a small amount was changed to sodium carbonate and sodium carbonate monohydrate.

The bands that appeared at 2950, 2825, and $2850cm^{-1}$ in some of the decomposed samples were of interest because they indicated the presence of carbon chains. In an attempt to isolate the compound giving rise to these bands several solvent extractions were performed. Portions of the heat decomposed sample were rinsed with benzene, hexane, or chloroform. The solvents were then evaporated onto a plate and the infrared spectrum of the residue was observed. In some instances the relative intensities of the $2900cm^{-1}$ bands were enhanced but we were unable to obtain samples free of carbonate absorptions. It seems that the substance producing these bands may either be bound to a carbonate type group or may not be appreciably more soluable than carbonates in the solvents used.

The electron spectra of a sample of heat decomposed sodium methylcarbonate showed peaks from sodium, oxygen and carbon. The sodium and oxygen peaks are singlets. There are at least
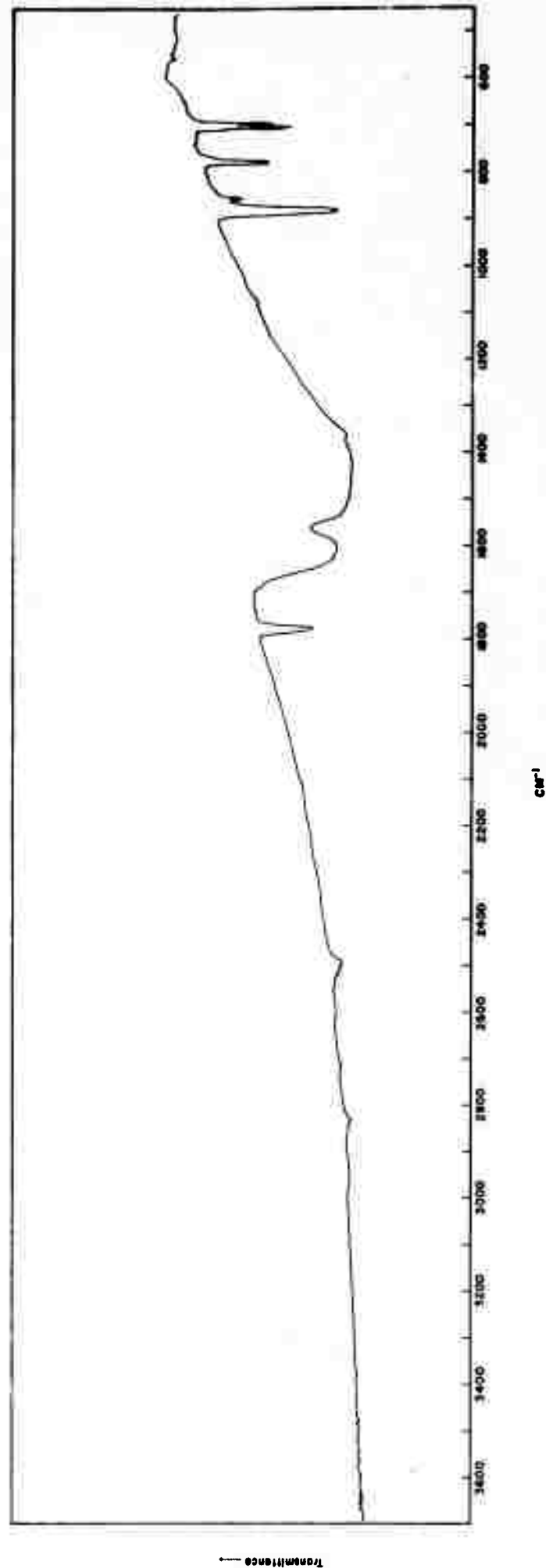
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Figure 6.   Infrared spectrum of a bulk sample of sodium methylcarbonate after standing in air for six weeks.

two types of carbon in the decomposed sample (Figure 7). One corresponds to a binding energy of a carbonate carbon. The other is in the energy range for a carbon with one bond to oxygen. The energy however, is lower than in sodium methyl-carbonate. In addition, there may be a hydrocarbon type carbon in the decomposed sample. The peak at 286eV (Figure 7) is relatively more intense than in sodium methylcarbonate (Figure 3).

Water

Since a number of spectra of anomalous water reported have some bands in the $2900cm^{-1}$ region (often at 2925 and $2850cm^{-1}$ as in decomposed sodium methylcarbonate) we investigated some of the possible sources.

A film was cast on an Irtran plate by evaporating deionized water, drop by drop, in the same manner as used for solutions from glass wool washings, etc. The preparation was continued for three days using, in all, about 2ml of water. The plate as run had some visible residue but there was no noticable difference between the infrared spectrum of the plate before and that of the plate after the water was evaporated. This experiment indicated that neither residue from the water nor contamination from the air during the preparation of the plate contributed to the infrared spectra of samples prepared in this way.

When room air was bubbled through 50ml of deionized water and the water evaporated on an Irtran plate, a very small but observable residue formed from <1ml of this solution. The infrared spectrum of this residue was extremely weak with two
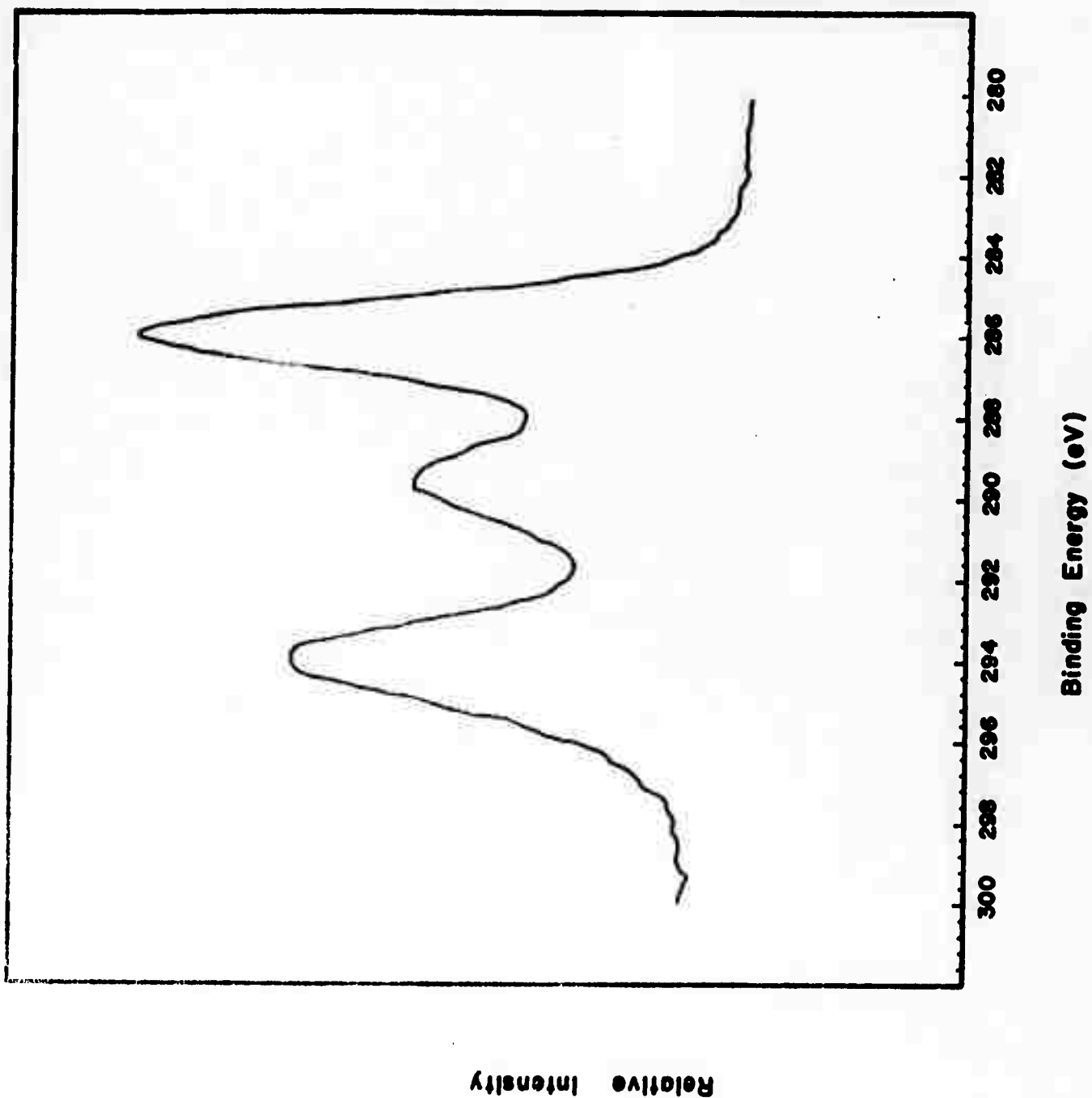
27

Figure 7. ESCA spectrum of the carbon region of a sample of sodium methylcarbonate after being heated at 80°C for one week.

bands at 2925 and 2850cm^{-1}.

Air Condensation

From the previous experiment it appeared that the room air might be the source of the compounds formed in the preparation of anomalous liquids. Therefore, a condensate was collected on the outside of a clean glass trap by filling the center with liquid nitrogen. The infrared spectrum of the residue from the evaporation of this condensate is shown in Figure 8. The bands at 1100, 1400, and 1600cm^{-1} are similar, in relative intensity and position, to those used to characterize anomalous water. The bands around 2900cm^{-1} are relatively more intense than those in anomalous water. The frequencies of the 2900cm^{-1} region bands are the same as those in decomposed sodium methylcarbonate. In addition, it was found that almost the same amount of residue and the same spectrum was observed whether a few drops of condensate were collected on the cold tube or a few ml were collected by scraping off the ice as it accumulated. When a plastic trap was used and the condensate was collected in plastic dishes, only trace amounts of residue were obtained from several ml of condensate.

Pyrex Wool

In the experiments with glass wool, presented earlier in this report, the wool, after being cleaned, was stored in a desiccator over water for several days before being rinsed. We repeated these experiments without storing the wool in the saturated atmosphere. Pyrex wool from a fresh roll was rinsed
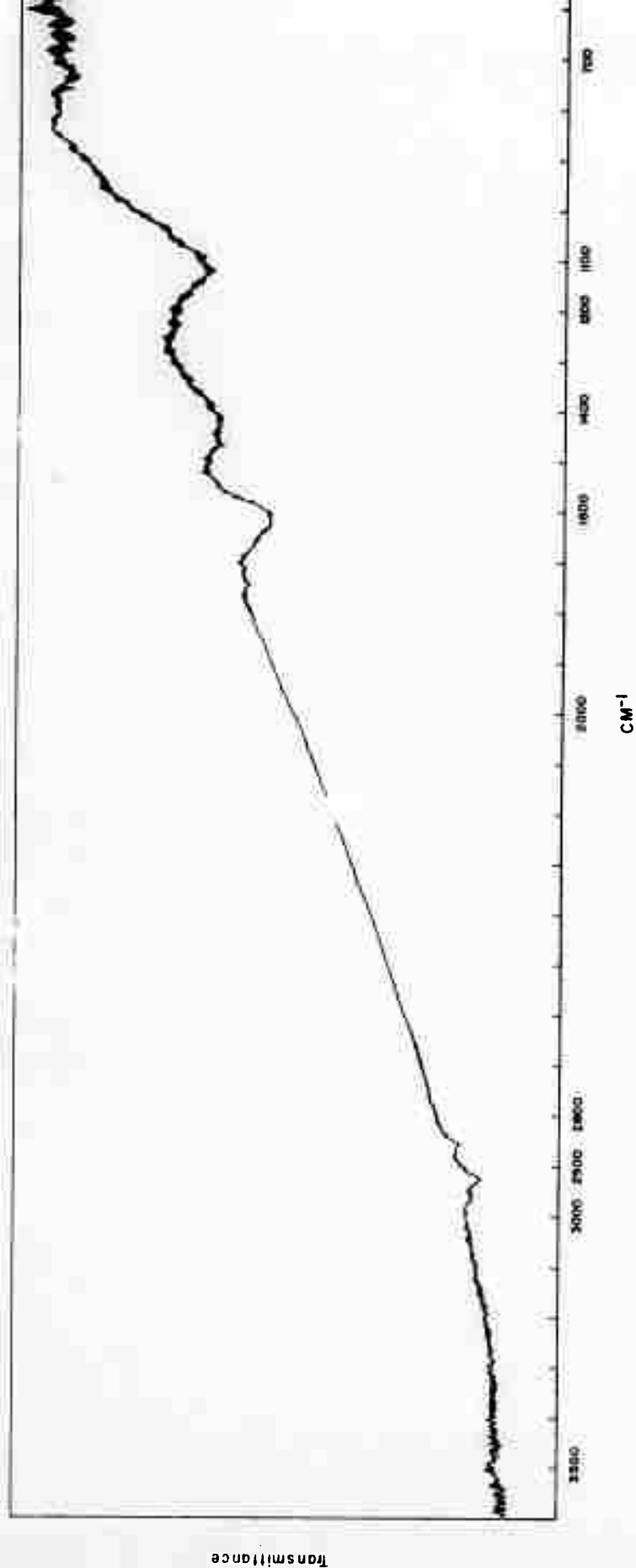
Figure 8. Infrared spectrum of material condensed on glass cold trap in room air.

with water and the water collected was evapoated to a residue. The infrared specturm of the residue is shown in Figure 9. It can be seen that the spectrum is quite similar to that of the residue from the pretreated Pyrex wool washing (Figure 1). The major difference seems to be the greater amount of nitrate in the non-treated sample and the greater amount of carbonates in the treated sample. When a sample of the residue from the water washings of untreated Pyrex wool was acidified with HCl, the infrared spectrum shows only weak absorptions at 2925, 2850 and $1600cm^{-1}$ and a broad band centered about $1100cm^{-1}$. Heating a sample of the residue left only sodium carbonate and nitrate ion. While most samples from the water washings of Pyrex are primarily carbonates and silicates, some samples are primarily nitrates. All of the washings seem to contain other compounds in lesser amounts. An electron spectrum of one sample indicated the presence of sodium, iron, oxygen, nitrogen, calcium, carbon, chlorine, boron, sulfur, and silicon. When quartz wool is washed with water, the primary band observed in the spectrum of the residue is due to silicates. It was observed that the less contact with glass in the quartz system the less carbonates formed.

Silicate

In studying the role of silicate in the formation of anomalous liquids, it was found that the spectrum of $Na_2SiO_3 \cdot 9H_2O$ can be substantially altered by carbon dioxide. A solution of $Na_2SiO_3 \cdot 9H_2O$ in water was prepared and some of the solution was evaporated onto an Irtran plate. The infrared spectrum of the residue is shown in Figure 10a. Pure CO_2 was then bubbled
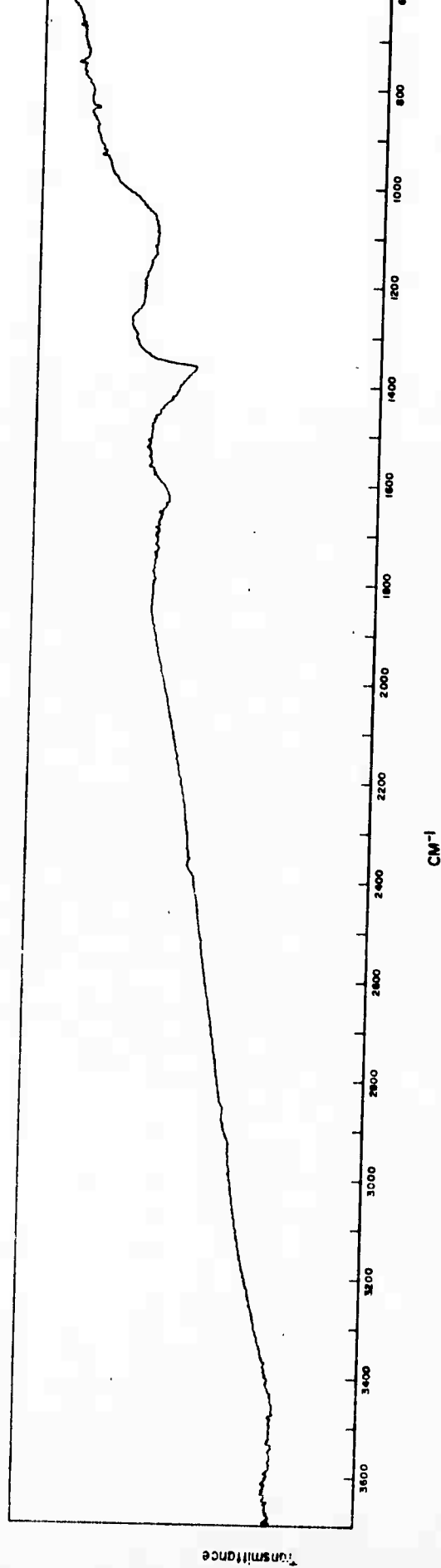
31

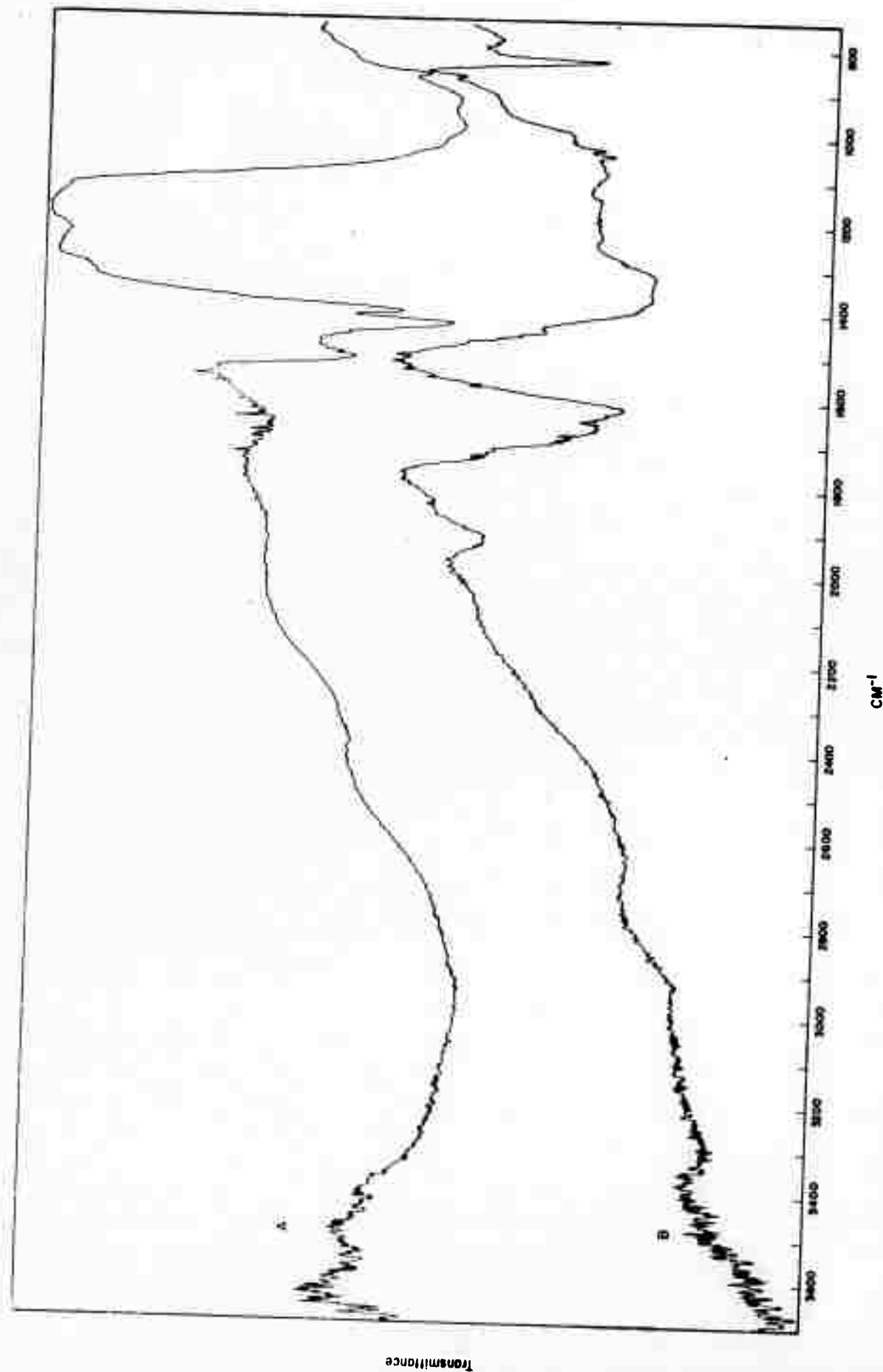Figure 5. Infrared spectrum of a water wash of Pyrex wool.

Transmittance

CM⁻¹

32

Figure 10. Infrared spectrum of residue from a solution of: a) $Na_2SiO_3 \cdot 9H_2O$ in water; b) $Na_2SiO_3 \cdot 9H_2O$ in water after bubbling CO_2 through solution.

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The infrared spectrum is shown in Figure 10b. It can be seen that the large silicate absorption centered at $980cm^{-1}$ in the original sample was shifted by the carbon dioxide treatment to $1050cm^{-1}$ and appears to be somewhat diminished in intensity.

Contamination

For a time during the course of these experiments, we were puzzled by the transformation of the infrared spectrum of sodium methylcarbonate (Figure 2) into that of Figure 11. This occurred in samples that were allowed to stand in desiccators for a long time (one to two weeks); or samples that had been obtained from Pyrex wool that had been extracted repeatedly and had thus been exposed to the air for at least several hours. A search carried on by Sadtler's of their infrared spectral files identified the compound as sodium trifluoroacetate.

Trifluoroacetic acid had been used in our laboratory in an entirely different study two years earlier, and amounts sufficient to give very clear and distinct IR spectra could still, surprisingly enough be obtained by prolonged exposure of certain materials, such as glass wool, to the air. In fact, we were able to crystallize sodium trifluoroacetate several times (but not at will) by dissolving sodium bicarbonate in methanol; filtering the solution, and placing a shallow layer of it in a beaker which was stored in a desiccator over drierite for twenty-four hours. After evaporation, the hydroscopic needles of F_3CCOO Na were found. Repeated
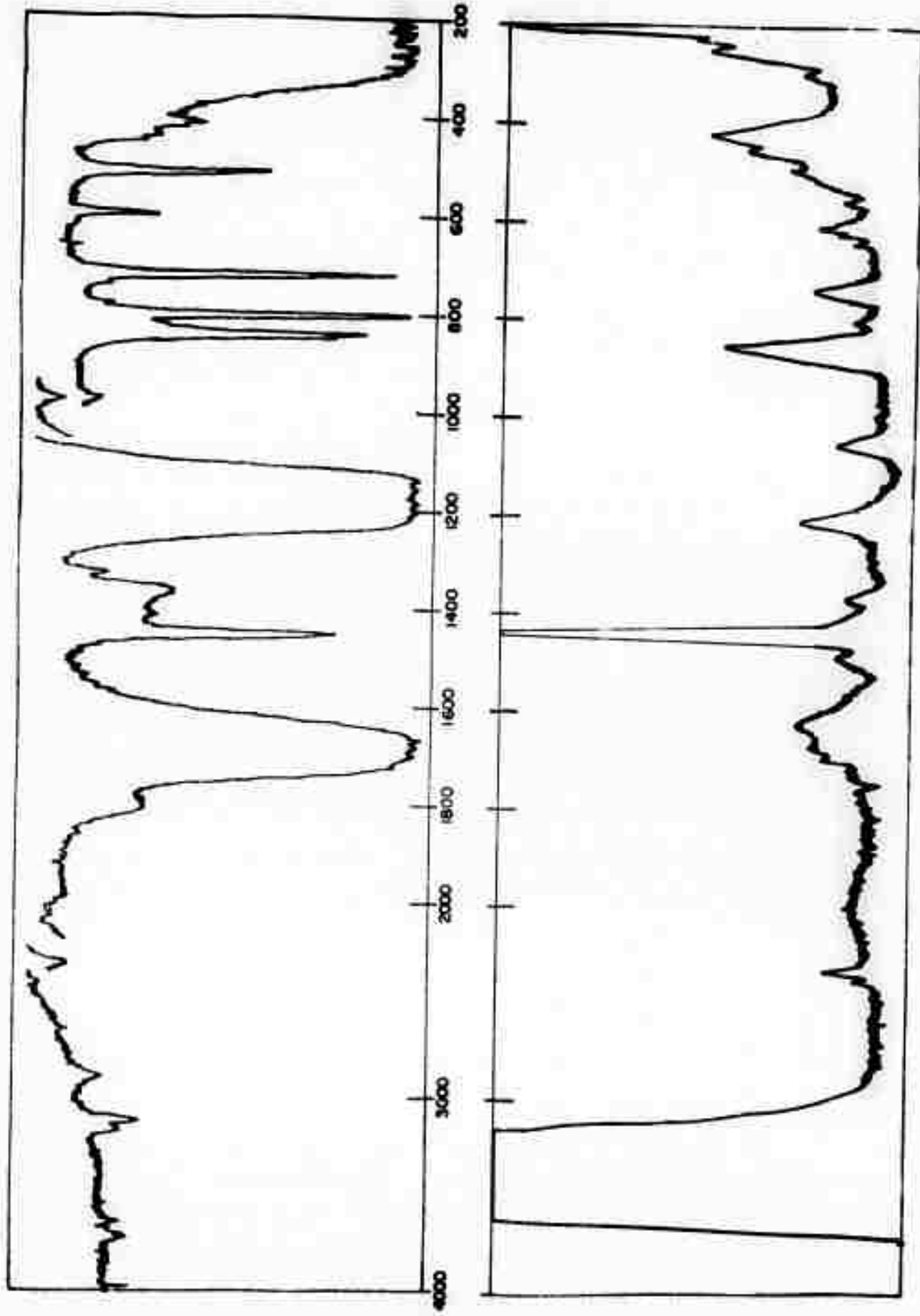
Figure 1.. Sodium trifluoroacetate. Upper: Infrared spectrum;
Lower: Raman spectrum.

tests showed that the starting materials - methanol and sodium bicarbonate - were free of trifluoroacetic acid and its salts. With time, we could collect less and less of the acetate and it eventually ceased to be a problem.

Discussion

When the research on this contract was begun, there was considerable controversy about the nature of anomalous columns formed in glass capillaries when exposed to an atmosphere saturated with water vapor. It was proposed that these columns were a polymeric form of water. Other researchers claimed that the anomalous substances were impurities from sweat, leaching of the glass, etc. Since only trace amounts were formed, elemental analyses were often contradictory. In these cases it was occasionally suggested that the different analyses could be explained by different compounds having been formed. The infrared spectrum became a criterion for comparison of compounds formed in different laboratories. An argument for the anomalous material being a polymer of water was that the spectra of the materials prepared in a number of different laboratories were very similar. Some proponents of impurity theories claimed that the spectrum of the anomalous material could be approximated by a variety of plausable impurities. Our approach to the problem was to try to identify the conditions of formation as well as any impurities. It was hoped that this would illustrate the nature of the anomalous substance and lead to the preparation of substantial quantities of the material.

We began our studies with thin capillaries since most material up to that time had been prepared by this method. These experiments seemed to indicate that a saturated atmosphere of water vapor and a relatively high area of glass surface were the primary requisites for the formation of anomalous substances. We then tried to prepare anomalous substances on glass wool because of the high surface area. It was during these experiments that we prepared sodium methyl-carbonate by rinsing glass wool with methanol. A plausible explanation for the formation of this substance was the interaction of the methanol with the sodium of the glass and the carbon dioxide of the air. If this explanation is correct, then it is probable that the anomalous substances formed with water may result from the interaction of water, glass, and air. The remainder of the experiments reported earlier were performed to test and characterize this theory.

The condensation from room air experiments showed two things. Since no observable anomalous material was formed on plastic surfaces, the role of glass was emphasized. The apparent lack of additional formation after the preparation of the first amounts of anomalous substance may indicate a deactivation, of sorts, of the glass surface during the reaction. The results of the washing of Pyrex wool with water show that the anomalous substance can be formed by the interaction of glass and air with liquid water as well as water vapor. The washing of quartz wool was not conducted in an all quartz system so the results may not be definitive. The low yields of anomalous material

from quartz might be due to the small amount of sodium in the system. The role of silicon in the formation of anomalous substances is not clear. The experiments with silicate inter-action with carbon dioxide (Figure 10) show that the infrared spectrum may not be a good method of determining the presence of silicates in anomalous samples. Our experience was that samples whose infrared spectra showed considerable amounts of silicon were glassier in appearance while those that were apparently free of silicon were more crystalline. Small amounts of a silicon compound may be necessary to produce the colligative properties observed.

From the results of our experiments we have formulated a theory for the formation of anomalous water and other anomalous substances. Substances on the surface of the glass (primarily ionic sodium), react with the first small amounts of the liquid condensed upon it to form basic site. This site then attracts and reacts with acidic substances from the air (primarily CO_2). Silicates from the surface may be involved and add to the non-crystalline properties. This theory provides a mechanism for the formation of similar anomalous materials in different laboratories since they would all have carbon dioxide in the laboratory air. In addition, the formation of sulfates and nitrates in some samples, even when there was no contact between these compounds and the sample, could be explained by the presence of oxides of sulfur and nitrogen in the air. In fact, in a chromatographic analysis of one of our samples, a peak attributable to nitrogen dioxide was observed. Hydrocarbons, which appear in most anomalous water samples even when steps are taken

to remove them from the glass, might also be condensed from the air (e.g. glass cold trap experiment, Figure 8). Some of the impurities that occasionally appear in samples might also be due only to casual contamination. The theory also accounts for the reported lack of formation of anomalous substances when several drops of water are placed in a capillary or when glass is soaked in water. A low liquid surface ratio is needed or only a very weakly basic solution will be formed. Reports of the formation of anomalous materials on surfaces other than glass (primarily magnesium oxide[14,15]) are explained by this theory. The only reasonable source of the compound was the laboratory air, and it was collected selectively in basic solutions.

It must be emphasized that we are advancing this explanation only as a theory and do not contend that it has been proved. The mechanism advanced explains the data we have collected during this research and some other data that has been reported in the literature. There are still several unanswered questions What is the structure of compounds formed by the interaction of the water, air and glass? The spectra and chemical reactions indicate carbonate or carbonyl type compounds but we have not explained the exact composition of "anomalous water." It is likely that the similarity of the infrared spectra of compounds prepared here with the spectra of those prepared in other laboratories (there are no reported spectra of Russian prepared anomalous material) indicates we are dealing with similar substances; there is little other proof. Some of these laboratories

have checked the properties of their samples with the properties reported by Russian workers. Thus it is likely that we are dealing with the same anomalous materials as the Russian workers. The reported preparation method of the Russians is also consistent with our theory. However, we cannot be one hundred percent sure we are dealing with the same material as the Russian workers.

An additional question that was raised during this investigation is what is the nature of the decomposition of sodium methylcarbonate. While the formation of sodium carbonate seems unreasonable, the apparent formation of methylene groups is puzzling. If indeed a chain hydrocarbon is formed at the low energies necessary to decompose methylcarbonate, this decomposition could be an interesting reaction.

CONCLUSION

Evidence from our own experiments and those reported in the literature point to the anomalous material being a product of the interaction of glass, air and water. The major portion of this material appears to be composed of sodium, oxygen, carbon, hydrogen and is largely inorganic.

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